

as originally filed

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### Thermoplastic molding compositions

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The invention relates to thermoplastic molding  
5 compositions based on ASA (acrylonitrile-styrene-  
acrylate) with improved flowability and improved  
extrusion properties. The invention further relates to  
a process for preparing these thermoplastic molding  
compositions, their use, and also, produced therefrom,  
10 reduced-gloss and antistatic films and moldings, and  
coatings with reduced gloss, and the use of these.

There is a wide variety of application sectors for  
thermoplastic molding compositions, and there is  
15 therefore a wide variety of known molding compositions  
with differing mixes for different application sectors.

EP-A 0 526 813 describes polymer blends for flexible  
films. These are made from a graft copolymer of vinyl  
20 monomers as graft shell on an acrylate rubber as graft  
base, a partially crosslinked copolymer rubber based on  
acrylate, an uncrosslinked polymer based on styrene  
compounds and/or on acrylic compounds and an ethylene-  
vinyl acetate copolymer. The plastic material which can  
25 be obtained, in which no PVC is present, is suitable  
for producing leather-like films. However, these  
mixtures tend to discolor undesirably during processing  
and have a disadvantageous relationship between tensile  
strength and elongation at break. Films of this type  
30 also exhibit relatively severe fogging when processed  
by methods similar to those conventionally used.

DE-A 31 49 358 relates to thermoplastic molding  
compositions obtainable from a graft copolymer with a

core made from a crosslinked alkyl acrylate and, if desired, comonomers and a shell obtainable by polymerizing a vinylaromatic monomer, with an ethylenically unsaturated monomer and with a copolymer  
5 obtainable by polymerizing a vinylaromatic monomer and with an ethylenically unsaturated monomer. Films produced from these thermoplastic molding compositions have the disadvantage of excessively low elongation at break together with excessively high hardness. Molding  
10 compositions of this type are moreover unsuitable for soft coextrusion compositions.

Plastic films with reduced-gloss surface and leather-like appearance are used, for example, for interior  
15 trim in motor vehicles, in the construction of buildings and in the sanitary and furniture sectors. The plastic usually used nowadays is PVC, mixed with a variety of vinyl polymers and plasticizers. These films are not fully aging-resistant at high temperatures, and  
20 they comprise volatile constituents and naturally contain halogen (see DE-A 42 11 415).

The use of alkylene oxide polymers (component (D)) in thermoplastic molding compositions is known.

25 AU-A 93 52 355 relates to thermoplastic synthetic mixtures for producing degradable single-use plastic products. These mixtures comprise from 65 to 95% by weight of high-molecular-weight polyethylene oxide, at  
30 least one high-molecular-weight thermoplastic polymer selected from the group consisting of nylon-11, nylon-12, polyethylene-co-acrylic acid, polyethylene-co-methacrylic acid, polyethylene-co-vinyl acetate and polyethylene-co-vinyl alcohol.

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EP-A 0 603 147 describes antistatic thermoplastic styrene (co)polymers which comprise high-molecular-weight polyethylene oxide (average molecular weight from 100,000 to 400,000), a lithium salt and ethylene glycol, diethylene glycol or triethylene glycol.

The use of alkylene oxide polymers in thermoplastic molding compositions based on SAN and/or ABS is disclosed in a number of documents.

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FR-B 1 239 902 describes the use of additives for rendering polymers antistatic. Examples of additives used are ethylene oxide-propylene oxide three-block copolymers. These antistats can be used in PVC, polymethacrylate, polyethylene, polystyrene or molding compositions made of ABS (acrylonitrile-butadiene-styrene).

EP-A 0 018 591 describes molding compositions which comprise styrene-acrylonitrile copolymers. These molding compositions also comprise linear three-block copolymers built up from two terminal ethylene oxide blocks and from a central propylene oxide block. The alkylene oxide three-block copolymers are used as lubricants. They affect the processing properties of styrene-acrylonitrile copolymers, in particular processing properties in injection molding. Adding the three-block polymers has no substantial effect on the mechanical properties.

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There has been no previous disclosure of the use of alkylene oxide polymers in molding compositions which comprise mainly ASA graft rubber with SAN, and comprise at least one olefin copolymer.

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It is an object of the present invention, therefore, to provide thermoplastic molding compositions which may be used either as films or else as soft, reduced-gloss surface coatings of hard, brittle or impact-resistant thermoplastics. These molding compositions are applied to coatings, for example by coextrusion, and for this have to have good flowability. A further object was to provide a process for preparing these thermoplastic molding compositions, as well as the use of the novel molding compositions for producing moldings or films, and as coextrusion compositions. The films should have reduced susceptibility to electrostatic charging and reduced Shore hardness. Further objects are the provision of films and moldings made from the novel molding compositions which have good and balanced mechanical properties, and the use of these.

We have found that this object is achieved by thermoplastic molding compositions, essentially comprising

(A) from 20 to 99% by weight of at least one graph copolymer, essentially obtainable from

(a1) from 30 to 90% by weight of a core, obtainable by polymerizing a monomer mixture, essentially consisting of

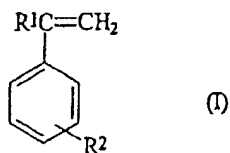
(a11) from 80 to 99.99% by weight of at least one C<sub>1</sub>-C<sub>10</sub>-alkyl acrylate,

(a12) from 0.01 to 20% by weight of at least one copolymerizable, polyfunctional, crosslinking monomer, and

(a13) from 0 to 40% by weight, based on the total weight of components (a11) and (a12), of at least one other copolymerizable, monoethylenically unsaturated monomer, and

(a2) from 10 to 70% by weight of a graft shell, obtainable by polymerizing a monomer mixture in the presence of the core (a1), and essentially consisting of

(a21) from 50 to 100% by weight of at least one styrene compound of the formula (I)



where  $\text{R}^1$  and  $\text{R}^2$ , independently of one another, are hydrogen or  $\text{C}_1\text{-C}_8\text{-alkyl}$  and/or of a  $\text{C}_1\text{-C}_8\text{-alkyl}$  (meth)acrylate, and

(a22) from 0 to 50% by weight of at least one monofunctional comonomer, and

(B) from 1 to 80% by weight of a copolymer obtainable from at least one alpha-olefin and from at least one polar comonomer, with the proviso that the monomers used are not vinyl acetate or any vinylaromatic monomer, and

(C) from 0 to 80% by weight of a thermoplastic polymer, obtainable by polymerizing a monomer mixture, essentially consisting of

(c1) from 50 to 100% by weight of at least one vinylaromatic monomer and/or of a C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylate, and

5 (c2) from 0 to 50% by weight of at least one monofunctional comonomer, and

(D) from 0.1 to 15% by weight of a three-block polymer made from

10

(d1) from 5 to 90% by weight of polyethylene oxide and

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(d2) from 95 to 10% by weight of polypropylene oxide

and having a central polypropylene oxide block with a molar mass of from 800 to 5 000 g/mol, and terminal blocks made from polyethylene oxide,

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where components A to D give 100% by weight in total.

These molding compositions feature excellent flowability and very good extrusion properties. They  
25 may be extruded to give films, or coated thermoformed sheets with a soft, mat surface, with consistent product quality or they may be processed to give moldings, for example by injection molding. The molding compositions have a high level of mechanical strength  
30 and heat resistance. They give good coextrusion. Films and moldings made from these molding compositions have reduced surface gloss and reduced electrostatic charging. They are suitable for internal trim of motor vehicles and for use in the construction of houses and  
35 in the sanitary and furniture sectors.

This type of combination of properties is achieved by the novel molding compositions. The fundamental properties here for application in films are achieved by the mixture of components (A) to (C) and the overall  
5 property profile for application in coextrusion is achieved by the mixture of components (A) to (D). As well as reducing susceptibility to electrostatic charging, component (D) improves flowability and reduces Shore hardness.

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The amount of component (A) present in the novel molding compositions, based on the total of components (A) to (D), is from 20 to 99% by weight, preferably from 30 to 98% by weight and particularly preferably  
15 from 60 to 95% by weight. This component is a particulate graft copolymer built up from an elastomeric graft core (a1) (soft component) and, grafted onto this, a shell (a2) (hard component).

20 The amount of the graft core (a1), based on component (A), is from 30 to 90% by weight, preferably from 35 to 80% by weight and particularly preferably from 40 to 75% by weight.

25 The graft core (a1) is obtained by polymerizing a monomer mixture made from, based on (a1),

(a11) from 80 to 99.99% by weight, preferably from 90 to 99.85% by weight and  
30 particularly preferably from 97 to 99% by weight, of at least one C<sub>1</sub>-C<sub>10</sub>-alkyl acrylate,

(a12) from 0.01 to 20% by weight, preferably from 0.2 to 10% by weight and  
35 particularly preferably from 0.5 to 5%

by weight, of at least one crosslinking monomer, and

5 (a13) from 0 to 40% by weight, preferably from 0 to 10% by weight based on the total weight of components (a11) and (a12), of at least one other copolymerizable, monoethylenically unsaturated monomer.

10 Particularly suitable C<sub>1</sub>-C<sub>10</sub>-alkyl acrylates [component (a11)] are methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, n-nonyl acrylate and n-decyl acrylate,  
15 and also mixtures of these, particularly preferably ethyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate or mixtures of these, and very particularly preferably n-butyl acrylate.

20 The copolymerizable, polyfunctional crosslinking monomers (a12) used are generally those which contain two, three or four, preferably two, copolymerizable double bonds which are not conjugated in 1,3 positions. Examples of monomers of this type suitable for  
25 crosslinking are ethylene glycol diacrylate, ethylene glycol dimethacrylate, butanediol diacrylate, butanediol dimethacrylate, hexanediol diacrylate, hexanediol dimethacrylate, divinylbenzene, diallyl maleate, diallyl fumarate, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, tricyclodecenyl acrylate,  
30 dihydrodicyclopentadienyl acrylate, triallyl phosphate, allyl acrylate, allyl methacrylate and dicyclopentadienyl acrylate (DCPA) (cf. DE-C-12 60 135).



Other examples which may be mentioned of copolymerizable, monoethylenically unsaturated monomers (component (a13)) are butadiene, isoprene;

- 5 vinylaromatic monomers, such as styrene or styrene derivatives of the formula I;

methacrylonitrile, acrylonitrile;

- 10 acrylic acid, methacrylic acid, dicarboxylic acids, such as maleic acid and fumaric acid, and also anhydrides of these, such as maleic anhydride;

- nitrogen-functional monomers, such as dimethyl-  
15 aminomethyl acrylate, dimethylaminoethyl acrylate, vinylimidazole, vinylpyrrolidine, vinylcaprolactam, vinylcarbazole, vinylaniline, acrylamide;

- C<sub>1</sub>-C<sub>4</sub>-alkyl methacrylates, such as methyl methacrylate,  
20 ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate and hydroxyethyl acrylate;

- 25 aromatic or araliphatic (meth)acrylates, such as phenyl acrylate, phenyl methacrylate, 2-phenylethyl acrylate, 2-phenylethyl methacrylate, benzyl methacrylate, benzyl acrylate, 2-phenoxyethyl methacrylate and 2-phenoxyethyl acrylate;

- 30 unsaturated ethers, such as vinyl methyl ether,

and also mixtures of these monomers.

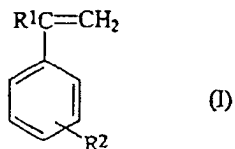
- 35 The amount of the graft shell (a2) present, based on component (A), is from 70 to 10% by weight, preferably

from 65 to 20% by weight, particularly preferably from 60 to 25% by weight, and it is obtainable by polymerizing a monomer mixture in the presence of the core (a1).

5

The graft shell (a2) is obtained by polymerizing a monomer mixture made from, based on (a2),

10 (a21) from 50 to 100% by weight, preferably from 55 to 95% by weight, particularly from 60 to 90% by weight, of at least one styrene compound of the formula (I)



15 where  $\text{R}^1$  and  $\text{R}^2$ , independently of one another, are hydrogen or  $\text{C}_1\text{-C}_8$ -alkyl and/or of a  $\text{C}_1\text{-C}_8$ -alkyl (meth)acrylate, and

20 (a22) from 0 to 50% by weight, preferably from 45 to 5% by weight, particularly preferably from 40 to 10% by weight, of at least one monofunctional comonomer.

25 The styrene compound used of the general formula (I) (component (a21)) is preferably styrene,  $\alpha$ -methylstyrene or ring- $\text{C}_1\text{-C}_8$ -alkyl-alkylated styrenes, such as p-methylstyrene or tert-butylstyrene, particularly preferably styrene or  $\alpha$ -methylstyrene.

30 According to the invention, the  $\text{C}_1\text{-C}_8$ -alkyl (meth)acrylates used are methyl methacrylate (MMA), ethyl methacrylate, n- or isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl

methacrylate, tert-butyl methacrylate, pentyl methacrylate, hexyl methacrylate, heptyl methacrylate, octyl methacrylate or 2-ethylhexyl methacrylate, particularly preferably methyl methacrylate, or mixtures of these monomers, methyl acrylate (MA), ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, tert-butyl acrylate, pentyl acrylate, hexyl acrylate, heptyl acrylate, octyl acrylate or 2-ethylhexyl acrylate, particularly preferably n-butyl acrylate, or else a mixture of these monomers with one another or with the methacrylates and/or styrene compounds of the formula I, where the amount of the acrylates in the graft shell is preferably subordinate.

15

Possible monofunctional comonomers (component (a22)) are monomers selected from the group consisting of methacrylonitrile, acrylonitrile and mixtures of these, N-C<sub>1</sub>-C<sub>8</sub>-alkyl-, N-C<sub>5</sub>-C<sub>8</sub>-cycloalkyl- and N-C<sub>6</sub>-C<sub>10</sub>-aryl-substituted maleimides, such as N-methyl-, N-phenyl-, N-dimethylphenyl- and N-cyclohexylmaleimide, and maleic anhydride. Acrylonitrile is preferred.

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It is preferable for the graft shell (a2) to have been built up from styrene or from a mixture comprising from 65 to 85% by weight of styrene, the remainder being acrylonitrile.

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In a preferred embodiment the graft shell (a2) is built up using a mixture of styrene (S) and acrylonitrile (AN) (molar ratio S/AN usually from 4.5:1 to 0.5:1, preferably from 2.2:1 to 0.65:1), styrene on its own, a mixture of acrylonitrile and methyl methacrylate (MMA) or MMA on its own.

30

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Component (A) is prepared by methods known per se, for example as described in DE-A 31 49 358.

For this, the core (a1) is first prepared, by  
5 polymerizing the acrylate(s) (a11) and the  
polyfunctional crosslinking monomers (a12), if desired  
together with the other comonomers (a13), in usually  
aqueous emulsion, in a manner known per se at from 20  
to 100°C, preferably from 50 to 80°C. Use may be made  
10 of the usual emulsifiers, such as alkali metal alkyl-  
or alkylarylsulfonates, alkyl sulfates, fatty alcohol  
sulfonates, salts of higher fatty acids having from 10  
to 30 carbon atoms, sulfosuccinates, such as Aerosol®  
OT (Cyanamid), ether sulfonates, such as Disponil®  
15 FES61 (Henkel) or resin soaps (Dresinate). Preference  
is given to the use of the sodium or potassium  
alkylsulfonates, or of salts of fatty acids having from  
10 to 18 carbon atoms.

20 The usual amounts of emulsifiers may be used.  
Advantageous amounts of emulsifiers are from 0.3 to 5%  
by weight, in particular from 1 to 2% by weight, based  
on the monomers used in preparing the core (a1).

25 The dispersion is preferably prepared using sufficient  
water to give the finished dispersion a solids content  
of from 20 to 60% by weight.

Preferred polymerization initiators are free-radical  
30 generators, for example peroxides, preferably  
peroxosulfates, such as potassium peroxodisulfate, and  
azo compounds, such as azodiisobutyronitrile. However,  
it is also possible to use redox systems, in particular  
those based on hydroperoxides, such as cumene  
35 hydroperoxide. Concomitant use may also be made of from  
0 to 3% by weight of molecular weight regulators, such

as ethylhexyl thioglycolate, tert-dodecyl mercaptan, terpinols or dimeric  $\alpha$ -methylstyrene.

5 The amount of the initiators generally depends on the desired molecular weight and is usually from 0.1 to 1% by weight, based on the monomers used in preparing the core (a1).

10 To maintain a constant pH, preferably from 6 to 9, buffer substances may be used as polymerization auxiliaries, for example  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  or sodium hydrogencarbonate. The usual amounts of the buffer substances are used, and further details in this connection are therefore unnecessary.

15 The precise polymerization conditions, in particular the type, method of addition and amount of the emulsifier, are generally determined individually within the ranges given above in such a way as to give  
20 the resultant latex of the crosslinked acrylate polymer (a1) a  $d_{50}$  of from 60 to 1000 nm, preferably from 80 to 800 nm, particularly preferably from 100 to 600 nm. The particle size distribution of the latex here should preferably be narrow.

25 The graft core (a1) may particularly preferably also be prepared by polymerizing the monomers (a11) to (a13) in the presence of a fine-particle latex made from elastomeric or hard polymers (seed-latex  
30 polymerization). The seed latex used may, for example, have been made from crosslinked poly-n-butyl acrylate or from polystyrene.

It is also in principle possible to prepare the graft  
35 core (a1) by a process other than emulsion polymerization, e.g. by bulk or solution

polymerization, and then to emulsify the resultant polymers. Microsuspension polymerization is also suitable, preferably using oil-soluble initiators, such as lauroyl peroxide or tert-butyl perpivalate. The processes for this are known.

In a preferred embodiment the core (a1) has a glass transition temperature below 0°C.

10 The graft-rubber particles (A) usually have a particle size ( $d_{50}$ ) of from 60 to 1500 nm, preferably from 100 to 1200 nm.

15 In a particularly preferred embodiment, graft-rubber particles (A) with a particle size ( $d_{50}$ ) of from 150 to 700 nm are used in order to give the molding composition high toughness.

20 In another preferred embodiment, a mixture of graft-rubber particles (A) of different sizes which has a bimodal particle size distribution is used. In a particularly preferred mixture of this type, from 0.5 to 99.5% by weight of the mixture has a particle size, as given by the average diameter ( $d_{50}$ ), of from 200 to 1000 nm, and from 0.5 to 99.5% by weight of the mixture has a particle size, as given by the average diameter ( $d_{50}$ ), of from 60 to 190 nm..

30 The chemical structure of the two graft copolymers is preferably the same, although the shell of the coarse-particle graft copolymer may in particular also have a two-stage structure.

35 The graft shell (component (a2)) is generally likewise prepared by known polymerization processes, such as emulsion, bulk, solution or suspension polymerization,

preferably in aqueous emulsion in the presence of an aqueous emulsion of the core (a1) (see DE-A 12 60 135, DE-A 31 49 358 and DE-C 11 64 080). In a preferred embodiment, the graft copolymerization is carried out  
5 in a system which is the same as that used for the polymerization of the core (a1) with addition, if required, of further emulsifier and initiator. These do not have to be the same as the emulsifiers or initiators used for preparing the core (a1). The  
10 emulsifier, the initiator and the polymerization auxiliaries may each be charged on their own or in a mixture to the dispersion of the core (a1). Any of the possible combinations of, on the one hand, charging and feeding and, on the other hand, initiator, emulsifier  
15 and polymerization auxiliaries may be used. Preferred embodiments are those known to the skilled worker. The monomer or, respectively, monomer mixture to be grafted on may be added to the reaction mixture all at once, batchwise in two or more stages or else continuously  
20 during the polymerization.

The amount of component (B) present in the novel molding compositions, based on the total of components (A) to (D), is from 80 to 1% by weight, preferably from  
25 60 to 3% by weight, particularly preferably from 50 to 4% by weight.

Alpha-olefins used to prepare component (B) may be C<sub>2</sub>-C<sub>8</sub>-alpha-olefins, such as ethene, propene, 1-butene,  
30 1-pentene, 1-hexene, 1-heptene or 1-octene, or mixtures of these, preferably ethene or propene.

Examples of polar comonomers, which according to the invention should not include vinyl acetate or  
35 vinylaromatic monomers, are:

alpha- or beta-unsaturated C<sub>3</sub>-C<sub>8</sub> carboxylic acids and the available anhydrides of these, for example acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, and glyceride esters thereof and also esters with C<sub>1</sub>-C<sub>8</sub>-alkyl alcohols whose alkyl radicals may have monosubstitution by phenyl groups or by naphthyl groups, unsubstituted or mono- or di-C<sub>1</sub>-C<sub>4</sub>-alkyl-substituted phenol or naphthol, methyl methacrylate, ethyl methacrylate, n-butyl acrylate, isobutyl acrylate, pentyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate, phenyl acrylate, phenylethyl methacrylate, phenylethyl acrylate, benzyl methacrylate, benzyl acrylate, phenylpropyl methacrylate, phenylpropyl acrylate, phenylbutyl methacrylate, phenylbutyl acrylate, 4-methylphenyl acrylate, naphthyl acrylate, phenoxyethyl methacrylate and phenoxyethyl acrylate;

methacrylonitrile, acrylonitrile;

carbon monoxide.

In a preferred embodiment, copolymers used as component (B) can be prepared from (I) 40 to 75% by weight of ethylene, from 5 to 20% by weight of carbon monoxide and 20 to 40% by weight of n-butyl acrylate, for example the commercially available ELVALOY<sup>®</sup> HP-4051 (DuPont), or preferably from (II) 50 to 98.9% by weight of ethylene, 1 to 45% by weight of n-butyl acrylate and 0.1 to 20% by weight of (meth)acrylic acid and/or maleic anhydride or from (III) 96 to 67% by weight of ethylene, 1 to 20% by weight of n-butyl acrylate, 3 to 10% by weight of (meth)acrylic acid and 0 to 3% by weight of maleic anhydride.



The copolymers (B) are prepared in a manner known per se (see US 2,897,183 and US 5,057,593). They are usually prepared by free-radical polymerization. The initiators usually used are peroxides, such as lauroyl  
5 peroxide, tert-butyl peracetate, tert-butyl peroxy-pivalate, di-tert-butyl peroxide, di(sec-butyl) peroxydicarbonate, tert-butyl peroctanoate and tert-butyl perisononanoate, preferably tert-butyl peroxy-pivalate and tert-butyl perisononanoate.  
10 Initiators containing azo groups, such as azobisisobutyronitrile, are also suitable.

The choice of the suitable initiator usually depends on the polymerization temperature to be selected, which is  
15 generally from 100 to 300°C, preferably from 130 to 280°C. The pressure during the polymerization is usually selected within the range from 100 to 400 MPa, preferably from 150 to 250 MPa. The amount of initiator is generally chosen within the range from 1 to 50 mol,  
20 preferably from 2 to 20 mol, for each  $10^6$  mol of the polar copolymer used.

The polymerization is generally carried out in a continuously operating tubular reactor. A reactor of  
25 this type is described, for example, in US 2,897,183. The reaction time is generally from 30 to 1 min, preferably from 5 to 2 min. The use of a solvent has hitherto been found to be optional.

30 The proportion of component (C), a thermoplastic polymer, in the molding compositions is from 0 to 80% by weight, preferably from 5 to 60% by weight, particularly preferably from 10 to 30% by weight, based on the total of components (A) to (D). This polymer is  
35 obtainable by polymerizing a monomer mixture essentially consisting of

(c1) from 50 to 100% by weight, preferably from 60 to 95% by weight, particularly preferably from 65 to 80% by weight, of at least one vinylaromatic monomer and/or of a C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylate, and

(c2) from 0 to 50% by weight, preferably from 0 to 40% by weight, particularly preferably from 5 to 35% by weight, of at least one monofunctional comonomer,

based in each case on component (C).

The vinylaromatic monomer (component (c1)) used comprises styrene, the substituted styrenes of the formula (I) mentioned above as component (a21) or the C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylates mentioned under component (a21), preferably methyl methacrylate. Preference is given to the use of styrene,  $\alpha$ -methylstyrene and p-methylstyrene.

Monomers which may be used as monofunctional comonomers (component (c2)) are those mentioned above as component (a22). The component (c2) used may also, if desired, be a mixture of the C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylates mentioned under component (a21) and the monomers mentioned under component (a21). Preference is given to monoethylenically unsaturated nitrile compounds, in particular acrylonitrile, methacrylonitrile and mixtures of these. Acrylonitrile is particularly preferred.

In a preferred embodiment use is made of a mixture of styrene (S) and acrylonitrile (AN), S and  $\alpha$ -methylstyrene, if desired mixed with methyl methacrylate or

with maleimides, or of methyl methacrylate, if desired with methyl acrylate. Particular preference is given to SAN polymers whose principal components are styrene and acrylonitrile.

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The polymers of component (C) are generally known. In some cases they are also commercially available, or can be prepared by known methods (see Kunststoff-Handbuch, Vieweg-Daumiller, Vol. V (Polystyrol), Carl-Hanser-Verlag, Munich 1969, page 118 et seq.). The polymerization is generally carried out by a free-radical route in emulsion, or in suspension, solution or bulk, and the latter two methods are preferred. The polymers (C) generally have viscosity numbers (VNs) (measured to DIN 53 726 on a 0.5% strength solution in dimethylformamide at 25°C) of from 40 to 160 ml/g, corresponding to average molar masses  $M_w$  of from 40,000 to 2,000,000.

20 The proportion of component (D) in the molding compositions, based on the total of components (A) to (D), is from 0.1 to 15% by weight, preferably from 0.2 to 12% by weight and in particular from 0.3 to 10% by weight. Component (D) is a three-block copolymer made from polyethylene oxide and polypropylene oxide and having a central polypropylene oxide block with a molar mass of from 800 to 5 000 g/mol and terminal blocks made from polyethylene oxide. The proportion of ethylene oxide is from 5 to 90% by weight, preferably from 10 to 80% by weight.

Component (D) is particularly preferably a three-block polymer having a portion of about 20% by weight of polypropylene oxide and a proportion of about 80% by weight of polyethylene oxide.

The molecular weights given are average molecular weights and are given as a number average  $M_n$  determined from the OH number in accordance with DIN 53240.

5 Component (D) is prepared by known polymerization processes, as described, for example, in N. Schönfeld, Grenzflächenaktive Ethylenoxid-Addukte, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1976, pp. 53  
10 et seq. This first produces a central polypropylene oxide block, to each of whose ends a block made from polyethylene oxide is added. The lengths of these two blocks do not have to be the same.

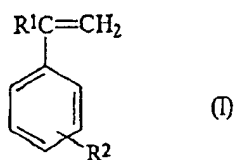
Besides components (A), (B), (C) and (D), the  
15 thermoplastic molding compositions may also comprise additives, such as lubricants, mold-release agents, pigments, dyes, flame retardants, antioxidants, stabilizers to protect against the action of light, fibrous or pulverulent fillers, fibrous or pulverulent  
20 reinforcing agents, and antistats in the amounts usual for these agents.

The invention also provides a process for preparing thermoplastic molding compositions in a manner known  
25 per se, by mixing, in a mixing apparatus,

(A) from 20 to 99% by weight of at least one graft copolymer, essentially obtainable from

30 (a1) from 30 to 90% by weight of a core, obtainable by polymerizing a monomer mixture, essentially consisting of

(a11) from 80 to 99.99% by weight of at least  
35 one  $C_1$ - $C_{10}$ -alkyl acrylate,



- 5                                where  $R^1$  and  $R^2$ , independently of one another, are hydrogen or  $C_1$ - $C_8$ -alkyl and/or                of                a                 $C_1$ - $C_8$ -alkyl (meth)acrylate, and
- 10                                (a22) from 0 to 50% by weight of at least one monofunctional comonomer, and
- 15                                (B) from 1 to 80% by weight of a copolymer obtainable from at least one  $\alpha$ -olefin and from at least one polar comonomer, with the proviso that the monomers used are not vinyl acetate or any vinylaromatic monomer, and with
- 20                                (C) from 0 to 80% by weight of a thermoplastic polymer, obtainable by polymerizing a monomer mixture, essentially consisting of
- 25                                (c1) from 50 to 100% by weight of at least one vinylaromatic monomer and/or of a  $C_1$ - $C_8$ -alkyl (meth)acrylate, and
- (c2) from 0 to 50% by weight of at least one monofunctional comonomer, and with

(a12) from 0.01 to 20% by weight of at least one copolymerizable, polyfunctional, crosslinking monomer, and

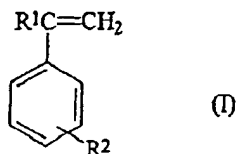
5 (a13) from 0 to 40% by weight, based on the total weight of components (a11) and (a12), of at least one other copolymerizable, monoethylenically unsaturated monomer, and

10

(a2) from 70 to 10% by weight of a graft shell, obtainable by polymerizing a monomer mixture in the presence of the core (a1), and essentially consisting of

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(a21) from 50 to 100% by weight of at least one styrene compound of the formula (I).



20 where  $R^1$  and  $R^2$ , independently of one another, are hydrogen or  $C_1$ - $C_8$ -alkyl and/or of a  $C_1$ - $C_8$ -alkyl (meth)acrylate, and

25 (a22) from 0 to 50% by weight of at least one monofunctional comonomer, with

(B) from 1 to 50% by weight of a copolymer obtainable from at least one  $\alpha$ -olefin and from at least one polar comonomer, with the proviso that the monomers used are not vinyl acetate or any vinylaromatic monomer, and with

30

(C) from 0 to 80% by weight of a thermoplastic polymer, obtainable by polymerizing a monomer mixture, essentially consisting of

5 (c1) from 50 to 100% by weight of at least one vinylaromatic monomer and/or of a C<sub>1</sub>-C<sub>8</sub>-alkyl (meth)acrylate, and

10 (c2) from 0 to 50% by weight of at least one monofunctional comonomer, and with

(D) from 0.1 to 15% by weight of a three-block polymer made from

15 (d1) from 5 to 90% by weight of polyethylene oxide and

(d2) from 95 to 10% by weight of polypropylene oxide

20 and having a central polypropylene oxide block with a molar mass of from 800 to 5 000 g/mol and terminal blocks made from polyethylene oxide,

where components A to D give 100% by weight in total,

25

and, if desired, with conventional additives.

The novel molding compositions may be prepared by mixing processes known per se, for example by melting  
30 in a mixing apparatus, e.g. an extruder, Banbury mixer or kneader, or on a roll mill or calender at from 150 to 300°C. It is also possible, however, for the components to be mixed "cold" without melting and for the mixture, composed of powder or pellets, not to be  
35 melted and homogenized until it is processed.

The novel thermoplastic molding compositions may be used to produce moldings, films or fibers. The invention therefore also provides the corresponding moldings, films and fibers.

5

The invention also provides the use of the novel thermoplastic molding compositions for coating sheet-like structures to give sheet-like structures with a reduced-gloss surface and antistatic properties, via  
10 coextrusion.

The novel molding compositions may be used to produce moldings of any type, in particular films. The films may be produced by extrusion, rolling, calendering or  
15 other processes known to the skilled worker, usually at from 150 to 280°C. Preference is given to the production of films from the molding compositions via extrusion. The novel molding compositions are molded here by heating and/or friction, on their own or with  
20 concomitant use of plasticizing or other additives, to give a processable film. Examples of equipment suitable for this purpose are extruders with slot dies. The films usually have a thickness of from 0.05 to 2 mm. An example of a process used to make finished products  
25 from films of this type is thermoforming at, for example, from 120 to 170°C.

In a preferred embodiment, coatings or leather-like films are produced by mixing

30

(A) from 20 to 99% by weight of at least one graft copolymer, essentially obtainable from

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(a1) from 30 to 90% by weight of a core, obtainable by polymerizing a monomer mixture, essentially consisting of



- (a11) from 80 to 99.99% by weight of n-butyl acrylate, and
- 5 (a12) from 0.01 to 20% by weight of tricyclodecenyl acrylate, and
- (a2) from 10 to 70% by weight of a graft shell, obtainable by polymerizing a monomer mixture in the presence of the core (a1), and essentially consisting of
- 10 (a21) from 60 to 90% by weight of styrene and
- 15 (a22) from 10 to 40% by weight of acrylonitrile, and
- (B) from 1 to 80% by weight of a copolymer, prepared from
- 20 from 67 to 96% by weight of ethylene, from 1 to 20% by weight of n-butyl acrylate, from 3 to 10% by weight of (meth)acrylic acid, and from 0 to 3% by weight of maleic anhydride, and
- 25 (C) from 0 to 80% by weight of a copolymer, prepared by continuous solution polymerization of
- (c1) from 65 to 85% by weight of styrene and
- 30 (c2) from 15 to 35% by weight of acrylonitrile, and
- (D) from 0.1 to 15% by weight of a three-block polymer made from
- 35

(d1) from 5 to 90% by weight of polyethylene oxide  
and

5 (d2) from 10 to 95% by weight of polypropylene  
oxide

and having a central polypropylene oxide block with a  
molar mass of from 800 to 5 000 g/mol and terminal  
blocks made from polyethylene oxide,

10

where components A to D give 100% by weight in total,

and then calendering or extruding to give films.

15 The novel molding compositions may also be used for  
coextrusion together with other polymers, giving  
coextruded moldings or coextruded films. Examples of  
these other polymers are ABS (acrylonitrile-butadiene-  
styrene polymers), PBT (polybutylene terephthalate),  
20 ASA (acrylonitrile-styrene-acrylate), PVC (polyvinyl  
chloride), SAN (styrene-acrylonitrile copolymers), MABS  
(methyl methacrylate-acrylonitrile-butadiene-styrene  
polymers), polymethyl methacrylate, polycarbonate and  
others.

25

Coextruded sheets may be further processed by  
thermoforming, for example for use in the sanitary  
sector, for producing containers (e.g. hard-shell  
suitcases) or for decorative purposes, e.g. in the  
30 furniture sector.

The coated sheet-like structures and the films with  
leather-like appearance have a wide variety of  
applications, in particular in the automotive industry  
35 for the construction of automotive interiors, for  
decorative purposes, as a leather substitute in

producing suitcases or bags and in the furniture industry as a coating material for the lamination of furniture surfaces, and also for the internal fitting-out of houses, aircraft, ships or trains, and in the  
5 sanitary sector.

The present invention therefore also provides the use of coated sheet-like structures or of films with a leather-like appearance for the internal fitting-out of  
10 houses, utility vehicles, aircraft, ships or trains, in the furniture industry and in the sanitary sector.

The molding compositions may moreover be coextruded to give tubes or profiles, and/or injection molded to give  
15 other moldings.

The novel thermoplastic molding compositions are preferably halogen-free. They are very substantially free from constituents which escape by evaporation or bleed-out, and exhibit practically no disadvantageous  
20 changes during processing, for example discoloration. In particular, even without the concomitant use of appropriate stabilizers or other additives, they have excellent heat-aging resistance and light resistance,  
25 and also good mechanical properties.

In particular, the novel molding compositions feature good flowability, especially when processed by extrusion. The good extrusion properties of the molding  
30 compositions bring about very consistent product quality of the films. These molding compositions are also antistatic and reduced-gloss to markedly matt.

#### **Examples**

35

The following constituents were prepared (all % given are by weight):

Preparation of a component A:

- 5           Particulate graft copolymer made from crosslinked poly-n-butyl acrylate (core) and styrene-acrylonitrile copolymer (shell)
- 10   A mixture made from 98 g of n-butyl acrylate and 2 g of dihydrodicyclopentadienyl acrylate and also, separately, a solution of 1 g of Na C<sub>12</sub>-C<sub>18</sub>-paraffin-sulfonate in 50 g of water were added at 60°C over the course of 4 hours to a mixture made from 3 g of a
- 15   polybutyl acrylate seed latex, 100 g of water and 0.2 g of potassium persulfate. The polymerization was then continued for a further 3 hours. The average particle diameter  $d_{50}$  of the resultant latex was 430 nm with a narrow particle size distribution ( $Q = 0.1$ ).
- 20   150 g of this latex were mixed with 60 g of water, 0.03 g of potassium persulfate and 0.05 g of lauroyl peroxide, and then firstly 20 g of styrene were grafted onto the latex particles over the course of 3 hours at
- 25   65°C, followed by a mixture of 15 g of styrene and 5 g of acrylonitrile over the course of 4 hours. The polymer was then precipitated by a calcium chloride solution at 95°C, separated off, washed with water and
- 30   dried in a stream of warm air. The degree of grafting in the polymer was 35% and the average diameter  $d_{50}$  of the particles was 510 nm.

The makeup of the graft copolymer was as follows (rounded values):

- 35   65% by weight of a graft core made from from polybutyl acrylate, crosslinked,

15% by weight of an inner graft made from styrene polymer, and  
20% by weight of an outer graft made from styrene-acrylonitrile copolymer with an S/AN weight ratio of  
5 3:1.

The seed polymer used at the outset was prepared by the process of EP-B 6503 (column 12, line 55 to column 13, line 22) by polymerizing n-butyl acrylate and  
10 tricyclodecenyl acrylate in aqueous emulsion, and had a solids of 40%.

The average particle size mentioned in describing component (A) is the weight average of the particle  
15 sizes.

The average diameter is the  $d_{50}$ , denoting that 50% by weight of all the particles have a smaller diameter, and 50% by weight a larger diameter, than the diameter  
20 corresponding to the  $d_{50}$ . To characterize the breadth of the particle size distribution the  $d_{10}$  and  $d_{90}$  values are frequently given in addition to the  $d_{50}$ . 10% by weight of all the particles are smaller, and 90% by weight are larger, than the  $d_{10}$  diameter. In a similar way, 90% by  
25 weight of all of the particles have a smaller diameter, and 10% by weight a larger diameter, than the diameter corresponding to the  $d_{90}$ . The quotient  $Q = (d_{90} - d_{10}) / d_{50}$  is a measure of the breadth of the particle size distribution. A smaller  $Q$  indicates a narrower  
30 distribution.

Component B:

A copolymer was prepared from 67-96% by weight of  
35 ethylene, 1-20% by weight of 4-butyl acrylate, 3-10% by

weight of acrylic acid and 0-3% by weight of maleic anhydride.

Component B is a product commercially available from  
5 BASF as a grade of Lupolen®.

Preparation of a component C:

Copolymer made from styrene and acrylonitrile

10

A copolymer made from 65% by weight of styrene and 35% by weight of acrylonitrile (component C) was prepared by continuous solution polymerization, as described in Kunststoff-Handbuch, ed. R. Vieweg und G. Daumiller,  
15 Vol. V "Polystyrol", Carl-Hanser-Verlag Munich 1969, pp. 122-124. The viscosity number VN (determined in accordance with DIN 53 726 at 25°C, 0.5% by weight in dimethylformamide) was 60 ml/g.

20 Component D:

The components (D) used was a three-block copolymer with a proportion of about 20% by weight of polypropylene oxide and a proportion of about 80% by  
25 weight of polyethylene oxide.

Component (D) is prepared by known polymerization processes, as described, for example, in N. Schönfeld, Grenzflächenaktive Ethylenoxid-Addukte, Wissenschaft-  
30 liche Verlagsgesellschaft mbH, Stuttgart, 1976, pp. 53 et seq. This first produces a central polypropylene oxide block, to each of whose ends a block made from polyethylene oxide is added. The lengths of these two blocks do not have to be the same.

35

Molding compositions prepared and their properties

Components A to D were intimately mixed, with melting, at 240°C and 250 rpm in a Werner + Pfleiderer ZSK30 twin-screw extruder, discharged and pelletized. The pellets were extruded in a Rheocord 90 single-screw 3:1 Haake extruder at 220°C and from 160 to 220 rpm to give a film of thickness 0.6 mm, using a slot die with 0.5 mm gap.

The following properties were determined for the films:

10

- Shore hardness: the Shore hardness was determined to DIN 43 505 using test apparatus D.

15

- The flowability of the molding compositions was determined on pellets, by measuring the melt volume rate (MVR) at 220°C or 200°C with a load of 10 kp or 21.6 kp. The amount discharged from a standard die in 10 min is given in ml.

20

The mixes for the films produced and the results of the tests are given in Table 1.

**Table 1**

Example/Component	1 (comparison)	2
A/pts. by wt.	70	70
B/pts. by wt.	20	20
C/pts. by wt.	10	10
D1/pts. by wt.	--	3
MVR 220/21.6/ml/10 min	41	108
MVR 200/21.6/ml/10 min	20	40
MVR 220/10/ml/10 min	<0.2	3.6
Shore D/°	41	31

The novel mixture is seen to have considerably better  
5 flowability and markedly lower Shore hardness.